

4.0 Groundwater Calibration Assessment Based on Partition Coefficients: Derivation and Examples

4.1 Introduction

Partition (or distribution) coefficient, K_d ,¹ values are utilized in transport and risk assessment modeling because of their simplicity in (1) understanding, (2) measuring, and (3) providing closed-form, explicit, analytical solutions to the advective-dispersive equations. Whelan (1996) presented a discussion that illustrates the inherent difficulties associated with utilizing partition coefficients as the sole parameter to define the geochemical properties of a solute as it migrates through a subsurface environment. Multiple definitions for K_d values have been identified, including those based on thermodynamics (*e.g.*, Gibbs free energy of formation), experiments (*e.g.*, batch and flow-through tests), and theory (*e.g.*, isotherms). Each of these procedures identifies a different value for the same parameter, which is supposed to describe the same phenomena. Although K_d values can be thermodynamically defined, their meaning becomes less clear in the real world. As such, K_d values can be estimated using transport models. This process, called calibrating a groundwater transport model to K_d values, involves treating the K_d value as the adjustable parameter (or dependent variable) while simulating known monitored contaminant data. Groundwater calibration captures the essence of the problem in the field. This is an iterative process that frequently requires that the magnitude of a number of other input parameters, such as effective porosity, dispersion, and flow rate, be adjusted to yield meaningful K_d values. A K_d value represents one of the calibration parameters because its magnitude is subject to not only the laboratory analyses but also to the heterogeneity in the field and different ways it is used in the mathematical constructs of different models.

4.2 Calibration: Location, Arrival Time, and Concentration

When calibrating a groundwater model to monitored information (*e.g.*, concentrations at a monitoring well), the model must predict the correct arrival time at the correct location, matching the magnitude of the monitored concentration. Therefore, time, location and magnitude are 3 crucial elements associated with any calibration exercise, and K_d impacts two of them (*i.e.*, travel time and magnitude). Location is predetermined by the user with respect to monitoring wells, receptor locations, *etc.* Once the distances have been defined, the calibration requires modifications to parameters that govern travel times and concentration levels. Parameters, which influence water and contaminant movement, are varied within acceptable ranges in an attempt to recreate conditions in the field. As the model complexity increases, the number of parameters that the analyst can vary increases, and the calibration process becomes increasingly more complicated. Figure 4.1 illustrates the relative relationships between input-data quality, output uncertainty, and types of problems addressed by each level of assessment. As Figure 4.1 indi-

¹ A list of acronyms, abbreviations, symbols, and notation is given in Appendix A. A list of definitions is given in Appendix B

cates, the computational requirements tend to be less at the earlier stages of an assessment when available data are less, and, correspondingly, the uncertainty with the output results tends to be greater. As the assessment progresses, improved site-characterization data and conceptualization of the problem increase, thereby reducing the overall uncertainty in risk estimates.

Figure 4.1 also illustrates some of the characteristics and relationships between screening-level (ranking), “analytical” (prioritization and preliminary assessments), and numerical (detailed) models.

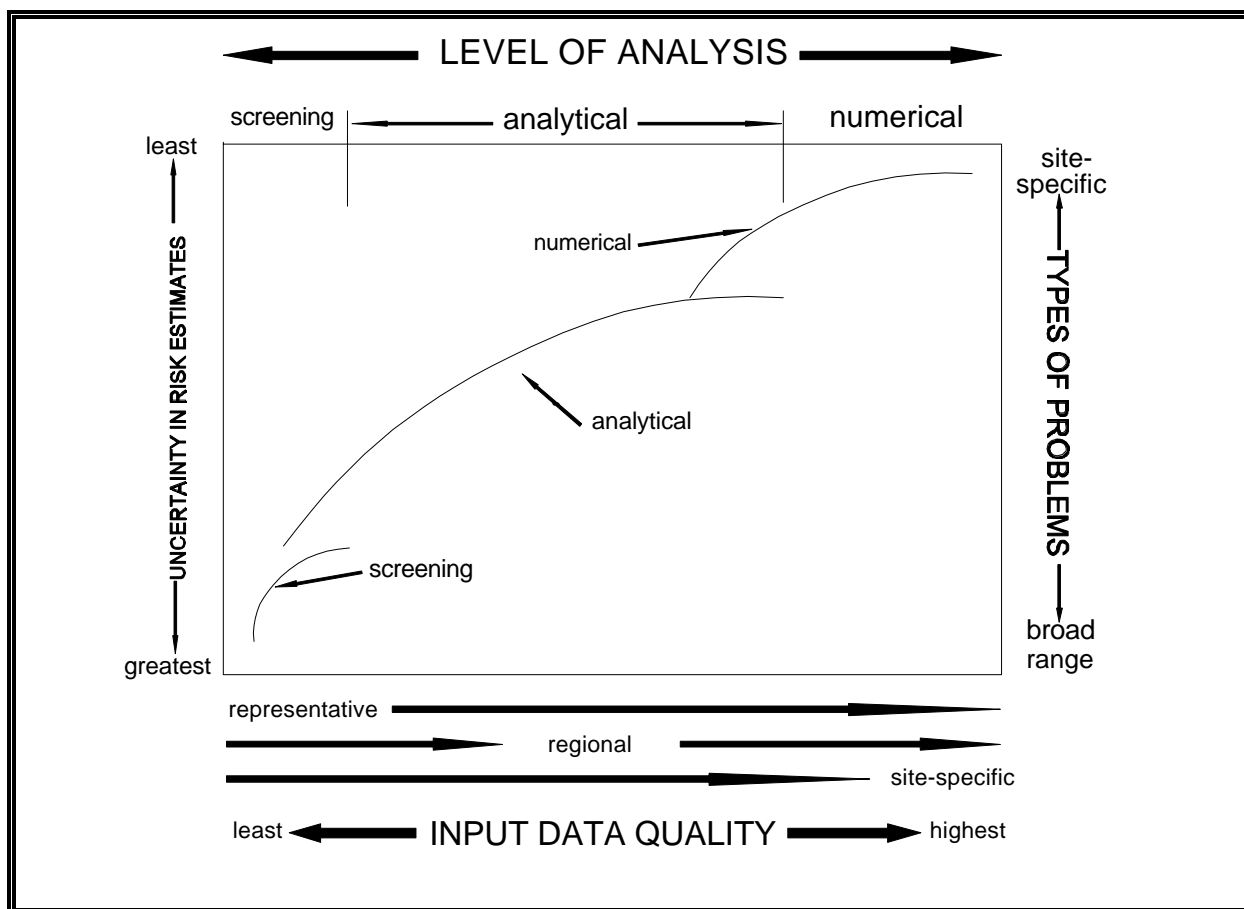


Figure 4.1. Relative relationships between input-data quality, output uncertainty, and types of problems addressed by each level of assessment.

Screening models are used to identify environmental concerns. These models, often based on a structured-value approach, are designed to be used with regional/representative information. Models such as the Hazard Ranking System (HRS) (EPA, 1984, 1992b) divide site and release characteristics into predetermined categories that are assigned a point value based on answers to questions. The score from such systems is useful to determine if a situation requires further analysis, but not to provide a method for estimating actual concentrations or impacts in the environment.

Detailed analyses require a highly specialized assessment of potential impacts. Detailed analyses are usually reserved for the most complex models, are data intensive, and are based on the expertise of the analyst. These detailed assessment models are used to address complex problems and concerns that are relatively well-defined. Models for detailed analyses tend to focus on special sets of problems and special types of situations. Although detailed assessment tools are appropriate for their intended application, extension beyond the site-specific application is often difficult or cost prohibitive. Typical models include MODFLOW (McDonald and Harbaugh, 1988) and CFEST (Cole *et al.*, 1988).

Analytically/semianalytically/empirically based models (designated as “analytical” models in Figure 4.1) can be utilized for prioritization or preliminary assessments and exist between initial-screening and highly specialized numerical models. These physics-based models are the most versatile as they do not have the data constraints associated with the numerical models. The analytical models may contain some numerical computations, hence the semianalytical designation. As Figure 4.1 illustrates, the analytical models are designed to provide environmental evaluations over a wide range of applications. Groundwater models that fall into this category include AT123D (Yeh, 1981), GROUND and GRDFLX (Codell *et al.*, 1982), and MEPAS (Buck *et al.*, 1995; Whelan *et al.*, 1992). The analytical-assessment models are codes with physics-based algorithms whose components can be utilized in a detailed (*i.e.*, numerical) or an initial-screening (*i.e.*, ranking/prioritization) assessment, where data and circumstances warrant.

The calibration process is an interactive one. Because data tend to be limiting, there are generally multiple ways in which parameters can be combined so the simulation results match monitored information. With increasing number of monitored data available, less combinations of the modeling parameters are possible to match the monitored information. In addition, many of these “matches” can assign unrealistic values to parameters; therefore, the number of acceptable possible combinations becomes even more limited. When calibrating, parameters can only be varied within ranges that physically make sense for the site and its conditions. If unrealistic output is a result of the analysis, then the (1) conceptual site model has to be re-evaluated, (2) input data must be re-examined, and/or (3) model must be re-evaluated to ensure that the assessment does not violate the assumptions, limitations, and constraints associated with the mathematical constructs of the code.

Each code has its own mathematical equations upon which it is based. A calibration exercise is performed to meet the constructs of these equations. Analytical models tend to be easier to work

with because of their closed-form, explicit solutions. With an analytical model, some initial calculations can be made that can provide an initial starting point for the calibration process; this process also illustrates how retardation factors (and ultimately K_d) influence the calibration process. As noted earlier, the intent of the calibration process is to get a contaminant from a source to the monitored location (*e.g.*, monitoring well) at the proper time with the appropriate concentration. In addition, the amount of mass monitored in the environment must be conserved, that is, the amount of mass predicted by the model to be in the environment should match the amount of mass monitored in the environment.

Travel times are influenced by the retardation factor, pore-water velocity, and dispersivity, although other parameters can also influence the outcomes. The retardation factor can be directly impacted by K_d . In the vadose zone, soil type and moisture content influence pore-water velocity, and in the saturated zone, soil type and effective porosity influence pore-water velocity. Longitudinal dispersivity normally influences the time to peak but by no more than 10 percent, although more is possible. Concentrations are generally influenced by the contaminant flux rate (or total mass released into the environment), mixing distances (dilution), pore-water velocity (dilution), retardation factor (K_d), and dispersivity (dispersion). If the size of the source is not well known, the areal extent of contamination influences concentration levels for spatially near-field problems. In any modeling exercise, the analyst will know some of the general characteristics of the parameters. Typically, the parameters that are used to calibrate the model are not known exactly; therefore, they can be modified within an appropriate range to help the analyst capture the essence of the problem.

4.3 Illustrative Calculations to Help Quantify K_d Using Analytical Models

If K_d forms the basic premise for retarding the movement of contaminants in a subsurface environment in the mathematical algorithms of a groundwater transport code, then the K_d permeates all of the contaminant transport calculations. Different computer codes may use different mathematical constructs, but the influence of K_d is usually very pronounced. The K_d value influences the calculations for determining the (1) contaminant travel time, (2) mass of contamination at the source or in a plume, and (3) distribution of the concentration in the environment. As an illustration of the impact that the K_d parameter can have in transport calculations, the influences of K_d on an analytical solution to the advective-dispersive equation are explored.

4.3.1 Governing Equations

The 1-dimensional advective, 3-dimensional dispersive equation with first-order degradation/decay can be expressed as follows:

$$\frac{\partial C_i}{\partial t} + v \frac{\partial C_i}{\partial x} = D_x^* \frac{\partial^2 C_i}{\partial x^2} + D_y^* \frac{\partial^2 C_i}{\partial y^2} + D_z^* \frac{\partial^2 C_i}{\partial z^2} - \lambda C_i \quad (4.1)$$

in which

$$v^* = \frac{v_p}{R_f} \quad (4.2)$$

$$v_p = \frac{v_d}{n_e} \quad (4.3)$$

$$R_f = 1 + \frac{\rho_b K_d}{n_e} \quad \text{saturated} \quad (4.4)$$

$$R_f = 1 + \frac{\rho_b K_d}{\theta_{vz}} \quad \text{vadose} \quad (4.5)$$

$$K_d = \frac{A_i}{C_i} \quad (4.6)$$

$$D^* = \frac{D_{\text{mech}} + D_{\text{mol}}}{R_f} \quad (4.7)$$

$$D_{\text{mech}} = \alpha v_p \quad (4.8)$$

where C_i = dissolved concentration
 v^* = contaminant velocity
 D^* = dispersion coefficient in the x, y, and z directions adjusted for retardation with the retardation factor
 λ = first-order degradation/decay coefficient
 v_p = pore-water velocity
 v_d = Darcy velocity
 R_f = retardation factor
 n_e = effective porosity
 ρ_b = bulk density
 θ_{vz} = moisture content in the vadose zone
 K_d = partition (distribution) coefficient
 A_i = adsorbed contaminant concentration on the soil particles
 D_{mech} = mechanical dispersion
 D_{mol} = molecular diffusion coefficient

α = dispersivity in the x, y, or z direction

The solution of advective-dispersive equation for an instantaneous release through a point source in a saturated zone, which is uniformly mixed in the vertical direction, at a distance (x) down gradient from the center of the source is as follows (Codell *et al.*, 1982; Fischer *et al.*, 1979; Whelan *et al.*, 1996; Yeh and Tsai, 1976; Yeh 1981):

$$C_i = \delta' X_{Gf} Y_{Gf} Z_{Gf} \quad (4.9)$$

where δ' = mass-related constant
 X_{Gf} , Y_{Gf} , and Z_{Gf} = Green's functions (which are orthogonal) in the x, y, and z directions, respectively
 X_{Gf} = Green's function corresponding to flow direction

in which

$$\delta' = \frac{M_{rel}}{R_f n_e} \quad (4.10)$$

$$X_{Gf} = \left(\frac{1}{4 \pi D_x^* t} \right)^{1/2} \exp(-\lambda t) \exp \left[- \left(\frac{(x - v_p^* t)^2}{4 D_x^* t} \right) \right] \quad (4.11)$$

$$Y_{Gf} = \left(\frac{1}{4 \pi D_y^* t} \right)^{1/2} \exp \left[- \left(\frac{y^2}{4 D_y^* t} \right) \right] \quad (4.12)$$

$$Z_{Gf} = \frac{1}{h_m} \quad (4.13)$$

where M_{rel} = released mass
 y = off-centerline distance
 h_m = mixing-zone thickness

and all other parameters retain their previous definitions.

The impact that the retardation factor and, hence, K_d has on the calculated value of the concentration at the receptor location can be profound, as illustrated by the number of locations that these terms appear in the governing equations.

4.3.2 Travel Time and the Partition Coefficient

As previously noted, it is very important to ensure that the contaminant arrives at the monitoring location at the appropriate time, and K_d can have a profound impact on the travel time. The advective travel time of the contaminant is defined as the distance x traveled divided by the contaminant velocity:

$$t_T = \frac{x}{v^*} \quad (4.14)$$

where t_T = total advective travel time of the contaminant

If a contaminant is traveling from a contaminated source through a vadose zone, through a saturated zone to a monitoring location, the total advective travel time is the summation of the travel times through the vadose (t_{vz}) and saturated (t_{sat}) zones:

$$t_T = t_{vz} + t_{sz} = \left(\frac{H_1 R_{f1}}{v_{p1}} \right) + \left(\frac{x_2 R_{f2}}{v_{p2}} \right) \quad (4.15)$$

where H_1 = thickness of the vadose zone
subscripts 1 and 2 = vadose and saturated zones, respectively

Substituting the definitions for retardation factor gives a slightly modified equation:

$$t_T = \frac{(H_1) \left(1 + \frac{\rho_{b1} K_{d1}}{\theta_{vz}} \right)}{v_{p1}} + \frac{(x_2) \left(1 + \frac{\rho_{b2} K_{d2}}{n_2} \right)}{v_{p2}} \quad (4.16)$$

This equation demonstrates the potential impact that K_d has on the travel time. Because K_d is assumed to be constant over the distanced traveled, a constant, ξ , can be defined, which represents the ratio of the partition coefficients between the vadose and saturated zones:

$$\xi = \frac{K_{d1}}{K_{d2}} \quad (4.17)$$

Substituting ξ into the total travel time equation gives the travel time as a function of the saturated zone's partition coefficient:

$$t_T = \left(\frac{H_1}{v_{p1}} \right) \left(1 + \left(\frac{\rho_{b1}}{\theta_{vz}} \right) \xi K_{d2} \right) + \left(\frac{x_2}{v_{p2}} \right) \left(1 + \left(\frac{\rho_{b2}}{n_{e2}} \right) K_{d2} \right) \quad (4.18)$$

Rearranging this equation and solving for K_{d2} gives:

$$t_T = \left(\frac{H_1}{v_{p1}} \right) + \left(\frac{H_1 \rho_{b1} \xi}{v_{p1} \theta_{vz}} + \frac{x_2 \rho_{b2}}{v_{p2} n_{e2}} \right) (K_{d2}) + \left(\frac{x_2}{v_{p2}} \right) \quad (4.19)$$

$$K_{d2} = \frac{t_T - (H_1/v_{p1}) - (x_2/v_{p2})}{\left(\frac{H_1 \rho_{b1} \xi}{v_{p1} \theta_{vz}} \right) + \left(\frac{x_2 \rho_{b2}}{v_{p2} n_{e2}} \right)} \quad (4.20)$$

This equation can be used to estimate initial values for the partition coefficients in the vadose and saturated zones, which will help ensure that the contaminant reaches the monitoring location at the appropriate time. These values can also be compared to literature or experimental values to see if they are consistent. If not, then the conceptual site model must be re-analyzed to ensure that the proper problem has been captured or that the appropriate data are being utilized.

4.3.3 Mass and the Partition Coefficient

The partition coefficient can be used to help estimate the mass of contamination that exists at the source or in a plume. The reported soil contamination in the vadose zone is usually expressed as the adsorbed concentration (A_i) and typically has units of mg/kg, which is also expressed as ppm (parts per 10^6). The aqueous concentration (C_i), using K_d as a conversion factor, can be calculated as follows:

$$C_i = \frac{A_i}{K_d} \quad (4.21)$$

The mass associated with the adsorbed phase in the vadose zone can be estimated as:

$$M_{ads} = V_{source} A_i (1 - n) \rho_{particle} \quad (4.22)$$

where M_{ads} = mass associated with the adsorbed phase in the vadose zone
 V_{source} = volume associated with the contaminated source
 n = total porosity
 $\rho_{particle}$ = particle density

The mass associated with the aqueous phase in the vadose zone can be estimated as:

$$M_{aq} = \frac{V_{source} A_i \theta_{vz}}{K_d} \quad (4.23)$$

where M_{aq} = mass associated with the aqueous phase in the vadose zone

The total mass associated with the vadose zone represents the summation of the mass associated with the adsorbed and aqueous phases, assuming no free product:

$$M_{\text{vadose}} = (M_{\text{ads}} + M_{\text{aq}})_{\text{vadose}} \quad (4.24)$$

where M_{vadose} = total mass associated with the vadose zone

The reported aqueous contamination in the saturated zone is usually expressed as the dissolved concentration C_i and typically has units of mg/l, which is also expressed as ppm (parts per 10^6). The mass associated with the aqueous phase in the saturated zone can be estimated as:

$$M_{\text{aq}} = V_{\text{source}} C_i n \quad (4.25)$$

The mass associated with the adsorbed phase in the saturated zone can be estimated as:

$$M_{\text{ads}} = V_{\text{source}} C_i K_d (1 - n) \rho_{\text{particle}} \quad (4.26)$$

The total mass in the vadose zone represents the summation of the mass associated with the adsorbed and aqueous phases, assuming no free product:

$$M_{\text{saturated}} = (M_{\text{ads}} + M_{\text{aq}})_{\text{saturated}} \quad (4.27)$$

where $M_{\text{saturated}}$ = total mass associated with the saturated zone

The total mass in the system is the summation of the masses in the vadose and saturated zones:

$$M_{\text{Total}} = M_{\text{vadose}} + M_{\text{saturated}} \quad (4.28)$$

If the environmental contamination in the vadose zone is expressed as a total mass in the waste site (or layer) per dry weight of soil, the dissolved and adsorbed concentrations can be calculated as follows (Whelan *et al.*, 1987):

$$C_i = \frac{C_{Tp} \rho_b}{\theta_{vz} + \rho_b K_d} \quad (4.29)$$

$$A_i = \frac{C_{Tp} \rho_b K_d}{\theta_{vz} + \rho_b K_d} \quad (4.30)$$

where C_{Tp} = total mass at the site per dry weight of soil

If the environmental contamination is expressed as a total mass per total volume of the waste site (or soil layer), the dissolved and adsorbed concentrations can be calculated as follows (Whelan *et al.*, 1987):

$$C_i = \frac{C_T}{\theta_{vz} + \rho_b K_d} \quad (4.31)$$

$$A_i = \frac{C_T K_d}{\theta_{vz} + \rho_b K_d} \quad (4.32)$$

where C_T = total mass at the site per total site volume

4.3.4 Dispersion and the Partition Coefficient

The 1-dimensional, dispersive equation in the lateral direction can be expressed as

$$\frac{\partial C_i}{\partial t} = D_y^* \frac{\partial^2 C_i}{\partial y^2} \quad (4.33)$$

where all of the terms are as previously defined. For an instantaneous release from a unit area in an aquifer of infinite lateral extent, the time-varying concentration as a function of lateral distance off the center line can be expressed as follows:

$$C_i = \left(\frac{M_A}{\sigma_{sd} (2 \pi)^{1/2}} \right) \exp \left[- \left(\frac{y^2}{2 \sigma_{sd}^2} \right) \right] \quad (4.34)$$

in which

$$\sigma_{sd} = \left(2 D_y^* t \right)^{1/2} = \left(\frac{2 D_y t}{R_f} \right)^{1/2} \quad (4.35)$$

$$D_y = \alpha_y v_p \quad (4.36)$$

where M_A = instantaneous mass released per unit area (*i.e.*, instantaneous point-source release)
 σ_{sd} = standard deviation associated with the Gaussian solution

Note that the standard deviation (*i.e.*, the degree of lateral spreading) is a function of the retardation factor and, hence, K_d .

To gain an understanding of the impact of the retardation factor (and K_d) on simple advective-dispersive systems, the impact of retardation at a location, x , can be discerned by substituting the time, t , with the advective travel time, as follows:

$$t = \frac{x R_f}{v_p} \quad (4.37)$$

$$\sigma_{sd} = (2 \alpha_y x)^{1/2} \quad (4.38)$$

The standard deviation that indicates the degree of spread at location x is independent of the retardation factor and K_d . This phenomenon is expected because when combined with flow in the longitudinal direction, advection impacts the effects of dispersion in the lateral direction. In effect, advection transports the contaminant in the longitudinal direction, so there is no infinite dispersion at any location in the lateral direction. Hence, Gaussian plumes grow as they migrate down gradient. Unlike the contaminant travel time, the dispersive phenomenon is not closely tied to K_d .

4.4 Modeling Sensitivities to Variations in the Partition Coefficient

Because the retardation factor and partition coefficient permeate many aspects associated with the mathematical algorithms for contaminant transport in the subsurface environment, K_d can have a significant impact on the outcome of any modeling exercise. Under certain circumstances though, K_d can have very little impact on the outcome. The next 2 sections discuss the conditions under which partition coefficients influence the outcome.

1. Relationship Between Partition Coefficients and Risk -- This section explores the situations under which variations in K_d can have a significant influence on simulated groundwater concentrations and, hence, risk.
2. Partition Coefficient as a Calibration Parameter in Transport Modeling -- This section presents an illustrative example of a calibration exercise where the calibration parameter is the partition coefficient.

4.4.1 Relationship Between Partition Coefficients and Risk

The K_d parameter potentially has a very large impact on the mobility of constituents in a subsurface environment. When combined with other phenomena (*e.g.*, degradation/decay, dispersion, pore-water velocity), K_d can have a significant impact by redistributing the contaminant both spatially and temporally.

For example, when the K_d parameter is sufficiently large, the contaminant moves slowly from the source to the receptor. Because significant levels of contaminant have not reached the receptor

within the receptor's lifetime, the risks over the lifetime are low. If the value of the K_d parameter is increased (*i.e.*, its mobility decreased even further), the risks are still low because the contaminant still has not reached the receptor. However, if the K_d parameter is sufficiently small, the contaminants arrive very quickly, and the receptors are exposed within their lifetime.

Different methods were presented in the previous section for determining K_d , and 4 different retardation factors were presented, which were based on K_d . Because different models use different formulations for the retardation factor, pore-water velocity, or contaminant velocity, the same K_d will produce different simulation results by the different models. As one can imagine, there are no accurate generalizations that can be made with regard to defining K_d ; as such, it tends to represent a calibration parameter in computer models. Because any modeling exercise (conceptually, physically, and mathematically) represents a simplification of the real world, many phenomena unknown or misunderstood are lumped into the parameters upon which modeling is based. K_d represents one of those parameters, where known and many unknown phenomena are lumped; as such, K_d tends to lose some of its meaning in the modeling world, although it retains its full meaning in the laboratory.

In the laboratory, K_d is determined under carefully controlled conditions; all aspects of the experiments are controlled to ensure accuracy in the experimental exercise. The real world does not afford the luxury of controlling the environment; therefore, the conditions surrounding the sorption phenomenon must be estimated. Unfortunately, site conditions may not be adequately described by sampling. Moreover, the identification of a single representative K_d value for a site may be impossible due to the large heterogeneities of the site's subsurface system.

4.4.2 Partition Coefficient as a Calibration Parameter in Transport Modeling

Calibrations do not necessarily ensure that the simulated results capture the essence of the transport phenomena. For example, Figures 4.2 and 4.3 present the results of a calibration using the MEPAS model to monitored data.¹ Each figure presents time-varying ^{90}Sr concentrations. Figure 4.2 presents MEPAS simulation with a K_d equaling 0.4 ml/g (*i.e.*, solid line and no symbols) and a simulation with K_d equaling 0.8 ml/g (*i.e.*, solid line with open triangles). The solid triangle represents the monitored data, identifying in a concentration of 220 pCi/l at year 27. As Figure 4.2 shows, the “0.8” calibration is precise and passes directly through the monitored data (*i.e.*, an exact match). The “0.4” simulation does not appear to capture the essence of the problem, as it predicts a concentration of 55,600 pCi/l at year 27. The “0.4” simulation seems to have over predicted the concentration by over 2 orders of magnitude. The significant difference in the peak concentration between the 2 simulations were the result of a minor change in K_d (*i.e.*, changes in the tenths place).

¹ The MEPAS simulations were based on actual site data published in Lewis *et al.* (1994) for the CERCLA hazardous waste site ST-19. Only the contaminant information was changed. Radionuclides were never present at the site; they are only used here as an illustrative example.

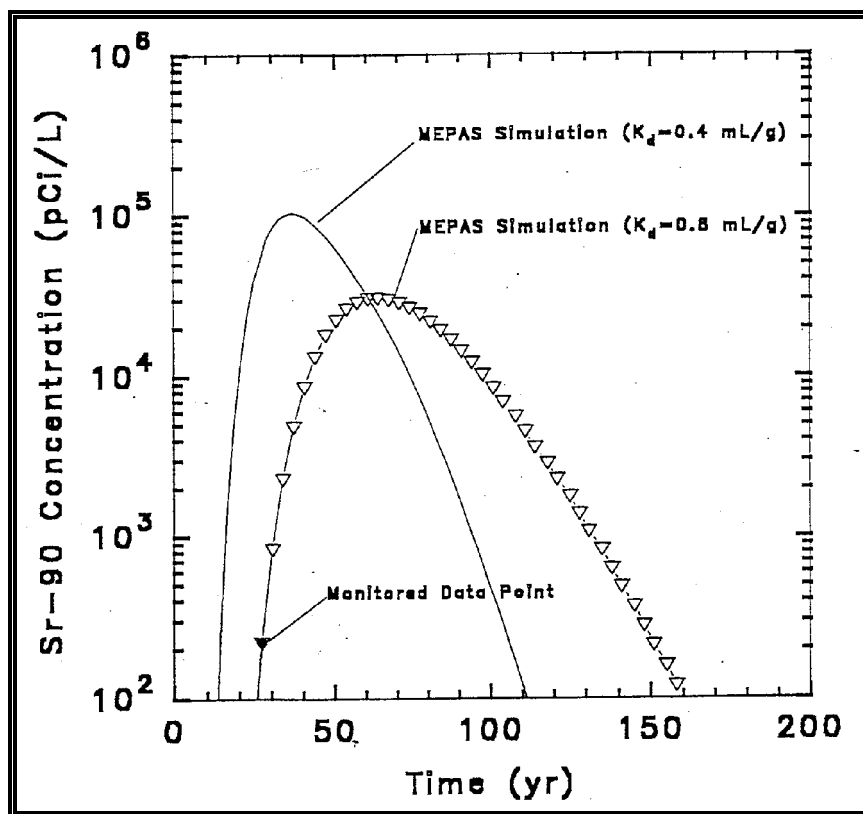


Figure 4.2. Example illustrating a MEPAS ^{90}Sr calibration with K_d equaling 0.8 mL/g and 1 monitored-data point.

Figure 4.3 presents the entire curve that is defined by monitored data, which includes the single data point from Figure 4.2. The monitored data in Figure 4.3 are presented as solid circular symbols. When all of the time-varying monitored data are considered in the assessment, the MEPAS simulation with a K_d equaling 0.4 mL/g appears to have captured the essence of the shape of the monitored data more accurately than the results associated with the 0.8 mL/g simulation. Although the “0.4” simulation does not precisely capture the entire shape of the monitored-data curve, it has captured the peak information, which usually is considered to be most important. Figure 4.3 illustrates the difficulty of calibrating a groundwater model to a single data point or a set of points that are not well distributed in time. Although the “0.8” simulation captured the single data point, it completely missed the peak concentrations and the time to peak. Because only 1 monitored data point is used in the calibration, an unlimited number of curves could have been simulated to pass through the monitored data point.

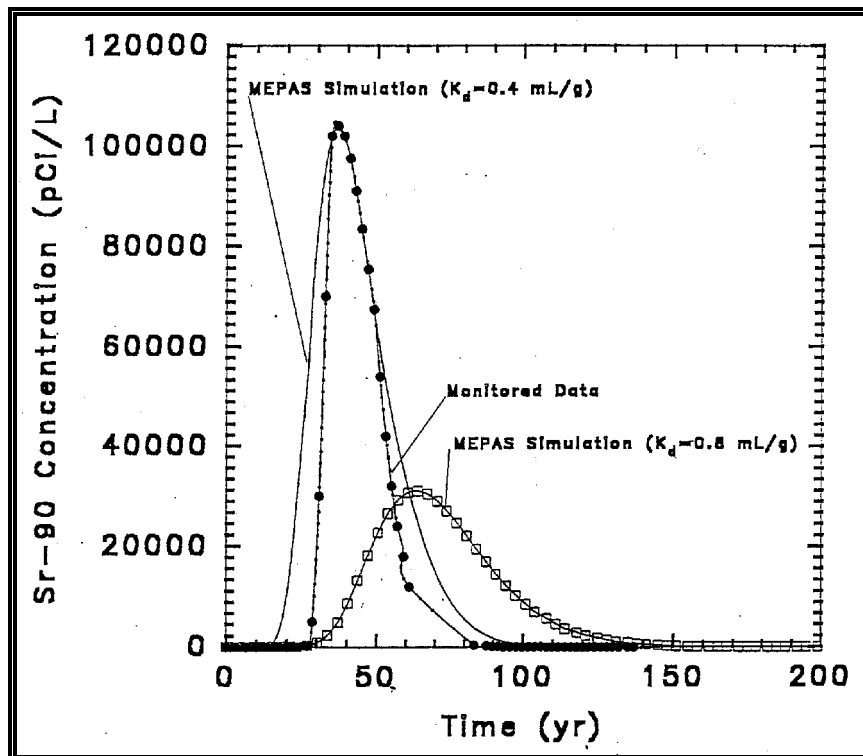


Figure 4.3. Example illustrating MEPAS ^{90}Sr calibrations with K_d equaling 0.4 and 0.8 mL/g and several monitored-data points.

Figure 4.3 illustrates that minor changes in K_d (*i.e.*, in the tenths place) can result in significant changes in simulation results. The concentrations between simulations at year 27 varied by over 2 orders of magnitude. The peak concentration decreased from 104,000 pCi/l to 31,000 pCi/l by increasing the K_d by only 0.4 mL/g. One simulation is over 5 times the drinking water limit of 20,000 pCi/l, while the other simulation is nearly equal to this limit. If the “0.8” results were assumed to be correct, the assessment would have underestimated the impacts by a factor of 3.4. Although the difference between 0.4 and 0.8 mg/l does not appear to be large, these results do illustrate the difficulties in using K_d and other parameters in the calibration process. These results also suggest that the discrepancy between “calibrated” simulations and limited data could be much larger (*i.e.*, orders of magnitude).

4.5 Summary

Various sections in this report have illustrated that there are many definitions for K_d (*e.g.*, theoretical, analytical, experimental, thermodynamic, *etc.*), all resulting with different values. The results presented in Figures 4.2 and 4.3 should represent a sobering reminder of the difficulties associated with groundwater assessments using partition coefficients. In many instances, a groundwater simulation is performed with no calibration at a site using K_d values that

have been obtained from “peer-reviewed” literature. The analyst tries to match soil types and environmental conditions with their site when “selecting” an appropriate K_d . It must be emphasized that these K_d values are unrelated to the actual site and only represent the laboratory conditions reported in the literature; they do not represent actual conditions at the site under investigation. The peer-reviewed values only provided an idea as to the possible magnitude associated with the K_d value. Different geochemical conditions, some known and unknown, exist between the actual site and those reported in the literature. The difficulty in using existing literature numbers is that the phrase “peer-reviewed literature” tends to lend too much credibility to these potentially inappropriate K_d values.